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Growth, nonlinear optical, thermal, dielectric and laser damage threshold studies of semiorganic crystal: Monohydrate piperazine hydrogen phosphate

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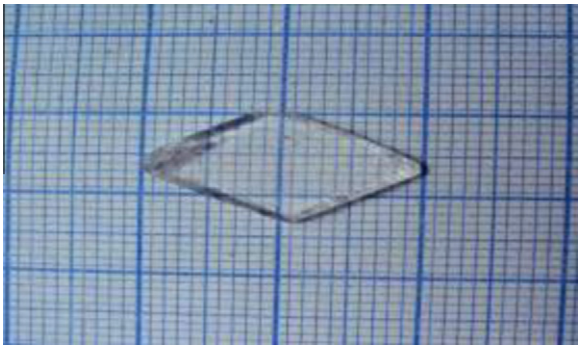
HIGHLIGHTS

- The lower cut off wavelength of the crystal is found to be 378 nm.
- SHG efficiency is 0.638 times that of KDP.
- The MPHP crystal exhibits higher laser damage threshold value than Urea and KDP.
- The crystal is thermally stable up to 135 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

Monohydrate piperazine hydrogen phosphate (MPHP), a semi organic nonlinear optical material has been synthesized and single crystals were grown from aqueous solution by slow evaporation technique. Single crystal X-ray diffraction study on grown crystal reveals that they belong to monoclinic crystal system with space group $P2_1/c$; (a = 6.39 Å; b = 12.22 Å; c = 11.16 Å; β = 97.14°; V = 864 Å^3). The structural perfection of the grown crystal was analyzed by high-resolution X-ray diffraction (HRXRD) rocking curve measurements. FTIR spectrum confirms the presence of the functional groups in synthesized material. UV–Vis spectrum indicates that the crystal is transparent in the entire visible region with a lower cut off wavelength of 387 nm. The variation of dielectric properties of the grown crystal with respect to frequency has been investigated at different temperatures. Thermal analysis carried out on the MPHP crystal shows that the crystal is stable up to 135 °C. Relative powder second harmonic generation efficiency tested by Kurtz–Perry powder technique, which was about 0.638 times that of Potassium dihydrogen phosphate.

Introduction

Nonlinear optical (NLO) material capable of generating the second harmonic frequency plays an important role in the domain of optoelectronics and photonics. Within the last decade, much progress has been made in the development of these NLO organic materials having large nonlinear optical coefficient. In the recent past, there have been extensive efforts to develop inorganic, organic and semi organic NLO crystals [1–4]. The key factor for material selection depends not only on laser conditions but also on the physical properties of the crystal, such as transparency, damage threshold, conversion efficiency, phase matching and temperature stability [5,6]. According to the Phillips–Van vechten–Levine Xue bond theory [7], constituent chemical bonds of the single crystal determine its NLO responses. Semiorganic materials structurally

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involve one or more kinds of hydrogen bonds which have been identified as one of the NLO functional bonds [4,8]. Therefore there are more chances to find new promising NLO single crystals in the semiorganic area.

Organic amines have had a tremendous impact on the chemistry of nano-porous materials during the past two decades, since the discovery of amines templated aluminium phosphates and transition metal phosphates [9–13]. In most cases, the amine is protonated as the chemical synthesis usually performed in acidic solution. In other cases, the amine can form a covalent bond to a metal and form a network compound, denoted as inorganic–organic hybrid materials where the amine can be considered to be part of the frame work [14].

Piperazine is a strong basic amine able to form a dication, in which all four N—H bonds are generally active in hydrogen bond formation. The monohydrate piperazine hydrogen phosphate compound consists of a framework of isolated PO_4 tertrahedra interleaved with piperazine and H_2O molecules [15]. The two amino groups of each piperazine molecule are protonated giving the formula $[N_2C_4H_{12}]^{2+}$. The stability of the frame work is ensured by strong O—H linkages between the O atoms from PO_4 tetrahedra and H atoms from the diamine and water molecules [15].

For molecular materials, it is assumed that the molecular structure, as well as the crystal packing arrangement, must also be noncentrosymmetric, unless a magnetic dipole or an electric quadrupole contributes to the bulk susceptibility [16–18]. Considering the SHG arising from bulk electric quadrupole and magnetic dipole effects and a surface dipole source, Lüpke presented a phenomenological theory [19]. The SHG in MPHP crystal is due to the weak interaction between the dipoles, which is easy for the ground state to turn into the excited state as a charge separated form, and generate the stable asymmetrical distribution of π-electron cloud density, thus exhibiting a minimum SHG effect [18,20].

In the present work, we have grown the MPHP crystal, studied the cell parameters using the single crystal XRD and analyzed using spectroscopic techniques. Furthermore, the variation of dielectric constant with frequency at different temperature was also investigated. The Kurtz–Powder technique reveals that the grown crystal has appreciable second harmonic efficiency.

Experimental

Material synthesis

MPHP was synthesised by the reaction between the Piperazine and orthophosphoric acid taken in the ratio 1:1. The calculated amount of piperazine was dissolved separately in the Millipore water. Orthophosphoric acid was added slowly to the piperazine solution with continuous stirring. The prepared mixture was stirred well for 5 h and clear solution was obtained. The solution was filtered off to remove insoluble impurities. Then the solution was allowed to evaporate at room temperature. Optically good quality single crystals were harvested from the mother solution in a week time and the photograph of the grown crystal is given in Fig. 1. The chemical reaction is as follows.

$$C_4H_{10}N_2 + H_3PO_4 \rightarrow [C_4H_{12}N_2]^{2+} \cdot [HPO_4]^{2-} \cdot H_2O$$

Solubility

The solubility test on MPHP in water was performed in the temperature range 32–50 °C. The temperature of the solution was maintained at the chosen constant temperature and continuously stirred using a motorized magnetic stirrer to ensure homogeneous temperature and concentration throughout the volume of the solution. The amount of MPHP required to prepare saturated solution at 32 °C was estimated and this process was repeated for different temperatures in the range of 32–50 °C. From the solubility curve presented in Fig. 2, it was found that the solubility of MPHP increases with the increase in temperature.

Characterization

Single crystal X-ray diffraction

The unit cell parameters of the grown MPHP crystals were obtained using ENRAF NONIUS CAD4/MAC4 X-ray diffractometer with Mo Kα (λ = 0.71073 Å) and presented in Table 1. These values agree well with the reported values [15]. Single crystal X-ray diffraction analysis shows that MPHP crystal belongs to the monoclinic crystallographic system with space group $P2_1/c$. The crystal packing, ORTEP diagrams and hydrogen bond geometry were generated using the data provided with CIF reference DU1011 in Ref. [15]. The hydrogen bond geometry is shown in Table 2. Figs. 3 and 4 show the crystal packing and ORTEP diagrams of the MPHP molecule with an atom numbering scheme.

The asymmetric unit of the crystal contains $C_4H_{12}N_2$ cation and HPO_4 anion with a water solvent. The molecular structure is stabilized by a weak intramolecular N—H···O hydrogen bond. The symmetry related molecules in the crystal packing are linked via intermolecular C—H···O, N—H···O and O—H···O interactions, to form a supramolecular two dimensional network (Table 2 and Fig. 4).

High-resolution X-ray diffraction studies

A multi-crystal X-ray diffractometers is used to study the crystalline perfection of the single crystal. The rocking curves of the crystals for the (200) diffraction planes were recorded in symmetrical Bragg geometry using the (100) natural facets by performing an ω scan [21] with triple-axis geometry. The monochromated X-ray beam incident on the specimen was obtained using a hybrid two-bounce Ge(220) monochromator with a parabolic multilayer mirror assembly. The diffracted beam from the specimen was detected using a scintillation detector with a triple-axis three bounce Ge(220) analyzer. Fig. 5 shows the high-resolution X-ray diffraction curve (DC) recorded for a typical BS specimen crystal using diffracting planes in symmetrical Bragg geometry by employing the MRD X-ray diffractometer described above with Cu Kα_1 radiation. As seen in the figure, the curve is not having a single diffraction peak. The solid line, which follows well with the experimental points (open circles) is the convoluted curve of three peaks using the Lorentzian fit. These peaks depict internal structural very low

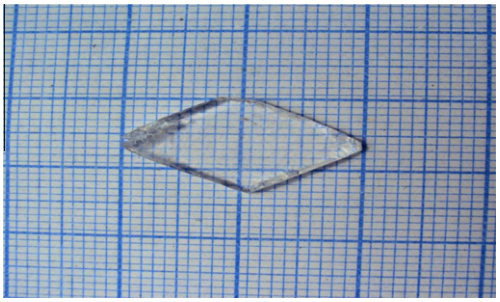

Fig. 1. Cut and polished MPHP single crystal.